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(54) CATALYST COMPOSITIONS ESPECIALLY USEFUL
 FOR PREPARATION OF UNSATURATED ACIDS

(71) We, THE STANDARD OIL COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of Midland Building, Cleveland, Ohio 44115, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a novel catalyst composition, which is particularly useful in oxidation reactions, such as the production of acrylic acid from acrolein and methacrylic acid from methacrolein.

The catalyst compositions of the invention comprise oxide complexes of vanadium, molybdenum and copper together with an additional metal oxide which may be antimony oxide or a mixture of antimony oxide and germanium oxide. As indicated these catalyst compositions are especially useful for producing acrylic acid from acrolein and for producing methacrylic acid from methacrolein.

Catalyst compositions similar to those of the invention are disclosed in Belgain Patent No. 773,851 which discloses catalysts of the composition molybdenum, vanadium, tungsten and antimony and one or more of the oxides of lead, silver, tin, titanium, copper and bismuth. U.S. Patent No. 3,736,354 discloses the catalyst compositions containing the oxides of vanadium, molybdenum and germanium and the oxides of vanadium, molybdenum and copper. German Patent No. 2,414,797 discloses a catalyst for the production of acrylic and methacrylic acids from acrolein or methacrolein which contains the metal oxides of molybdenum, vanadium, copper and at least one element of the group of iron, cobalt, nickel and magnesium. U.S. Patent No. 3,725,472 discloses a catalyst for the oxidation of α , β -unsaturated carbonylic compounds to the corresponding unsaturated acids employing a catalyst containing the oxides of molybdenum, vanadium and antimony.

None of the foregoing patents, however, disclose the catalyst compositions of the present invention or the fact that unexpectedly high yields of unsaturated carboxylic acids are obtained from the corresponding unsaturated aldehydes in the presence of these catalysts.

As indicated, the catalyst composition according to the invention comprises a catalyst having the empirical formula



wherein X is antimony or a mixture of antimony and germanium,

a is a number from 6 to 18,

b, c and d are each 0.1 to 6 and

e is the number of oxygen atoms required to satisfy the valence requirements of the other elements present.

These catalyst compositions are especially effective for preparing acrylic acid from acrolein and the preparation of methacrylic acid from methacrolein. The catalyst compositions are also highly effective for oxidation reactions such as the oxidation of butadiene to maleic anhydride and the oxidation of the butenes and the aromatics to various oxygenated compounds. The catalyst compositions of the present invention are highly reactive and are capable of catalysing very selectively the oxidation of acrolein to acrylic acid, with little acetic acid being formed.

The catalysts of the invention may be prepared by mixing the catalyst forming ingredients in the proper proportions, preferably in an aqueous mixture and drying the resulting aqueous slurry with or without a reducing agent, and calcining the product. The ingredients employed in the preparation of the catalysts can be the oxides, halides, nitrates, acetates or other salts of the particular compound added, and particularly preferred is the use of water soluble salts of the metal components. If a support is used, the material comprising the support may be incorporated into the catalyst along with the other ingredients or the catalytic ingredient may be coated on an inert core. After the catalyst ingredients have been combined to form an aqueous slurry, the slurry is evaporated to dryness, and the dried solid obtained is heated in the presence of air at temperature between about 200° and 600°C. This calcination can take place outside of the catalytic reactor or an *in situ* activation could be utilized.

In addition to the active catalytic ingredients the catalysts of the invention may contain a support material. Suitable support materials include silica, alumina, zirconia, titania, silicon carbide, boron phosphate and the like. A preferred support material is Alundum (Registered Trade Mark). Also contemplated in this invention is the incorporation of metal oxide promoters in the catalyst compositions to enhance further their activity.

As noted above, the catalyst of the invention are useful in a number of different oxidation reactions. Preferred among these reactions is the production of unsaturated acids from the corresponding unsaturated aldehydes. In such a process, acrylic acid or methacrylic acid is produced by reacting acrolein or methacrolein with molecular oxygen in the presence of steam at a temperature of about 200° to about 500°C. Of special interest is the preparation of acrylic acid from acrolein because of the extremely desirable results obtained.

The oxidation of unsaturated aldehydes to obtain the corresponding acid is well known in the art. Basically, the invention, with respect to the process, is the use of the new catalyst within the parameters of the known art process.

The known process involves the contacting of the unsaturated aldehyde with molecular oxygen in the presence of steam at a temperature of 200°C to 500°C. The ratio of the reactants may vary widely with molar ratios of molecular oxygen to aldehyde of about 0.5 to about 5 moles normally being employed. Molecular oxygen is most conveniently added as air. The amount of steam may vary widely from the small amount generated in the reaction to 20 or more moles of steam per mole of aldehyde. In the preferred practice of the invention 1 to 10 moles of steam are added to the reactant feed.

The reaction may be conducted in a fixed- or fluid-bed reactor using atmospheric, superatmospheric or subatmospheric pressure. The apparent contact time may vary considerably with contact times of a fraction of a second to 20 seconds or more normally being employed.

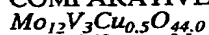
The following Examples illustrate the invention:-

COMPARATIVE EXAMPLES A - C AND EXAMPLE 1

The catalysts of the invention were prepared and compared to the known catalyst compositions of U.S. Patent No. 3,736,354 (Examples A & B), U.S. Patent No. 3,725,472 (Example C) and German patent No. 2,414,797 (Example D) for the reaction of the oxidation of acrolein to acrylic acid.

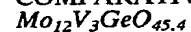
The catalysts of the comparative examples were prepared as follows.

COMPARATIVE EXAMPLE A



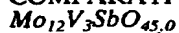
To 250 cc of hot distilled water was added 6.88 g of ammonium metavanadate. After approximately 15 minutes of heating and stirring, the reagent was dissolved and 41.54 g of ammonium heptamolybdate was added to the solution. The ammonium heptamolybdate and 1.96 g of cupric acetate which was added subsequently, dissolved almost immediately. The solution was evaporated to near dryness with continual stirring and the catalyst was then placed in a drying oven at 110°C-120°C for 16 hours. The dried material was crushed and ground through a 50 mesh screen. A sufficient amount of catalyst was employed to coat 3/16 spheres to achieve a twenty weight percent coating on the spheres. The coated spheres were then dried at 110°-120°C for three hours and then activated by heat treating at 370°C for two hours.

COMPARATIVE EXAMPLE B



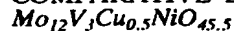
The procedure of comparative Example A was repeated with the exception that 6.67 g of ammonium metavanadate and 40.27 g of ammonium heptamolybdate were used, and 1.99 g of germanium dioxide was employed in place of the copper acetate.

COMPARATIVE EXAMPLE C



The procedure of Comparative Example A was repeated using 6.54 g of ammonium metavanadate and 39.50 g of ammonium heptamolybdate, and 2.71 g antimony oxide (Sb_2O_3) was employed in place of the copper acetate.

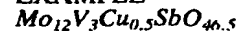
COMPARATIVE EXAMPLE D



The procedure of Comparative Example A was repeated using 6.61 g of ammonium metavanadate, 39.93 g of ammonium heptamolybdate, 1.88 g of cupric acetate and 5.47 g of nickel nitrate hexahydrate, these ingredients being added to the aqueous solution in that order.

The preparation of the catalysts in the Examples representative of the invention are given below.

EXAMPLE



To 250 cc of hot distilled water was added 6.38 g of ammonium metavanadate. After approximately 15 min. of heating and stirring, the reagent was dissolved and 38.49 g of ammonium heptamolybdate was added to the solution. The ammonium heptamolybdate, and 1.81 g of cupric acetate which was added subsequently dissolved almost immediately. 2.64 g of antimony oxide (Sb_2O_3) was added and the solution was evaporated to near dryness with continual stirring. The catalyst was then placed in a drying oven for 16 hours at 110-120°C and the dried material was crushed and ground to pass through a 50 mesh screen.

A sufficient amount of catalyst was employed to coat 3/16" spheres of Alundum to achieve a twenty weight percent coating on the spheres. The coated spheres were then dried at 110-120°C for three hours and then activated by heat treating at 370°C for two hours. The catalysts prepared above were placed in a fixed bed reactor constructed of a 1.0 cm. inside diameter stainless steel tube having a reaction zone of 20 cc. capacity. The reactor was heated in a split block furnace. The reactor was fed with a mixture of acrolein/air/ N_2 /steam in the molar ratio of 1/8.5/2.5/6. The apparent contact time was 2 seconds. The temperature of the surrounding block is given in Table 1. The results are also given in Table 1 using the following definitions:

35	Single Pass Yield, % =	$\frac{\text{Moles of product recovered} \times 100}{\text{Moles of acrolein fed}}$	35
	Conversion, % =	$\frac{\text{Moles of acrolein reacted} \times 100}{\text{Moles of acrolein fed}}$	
40	Selectivity, % =	$\frac{\text{Moles of acrylic acid recovered} \times 100}{\text{Moles of acrolein reacted}}$	40

TABLE I

Oxidation of acrolein to acrylic acid

Example	Catalyst (1)	Temp., °C	% Single Pass Acrylic Acid	Yield Acetic Acid	% Conversion	% Selectivity
Comp. A	$\text{Mo}_{12}\text{V}_3\text{Cu}_{0.5}\text{O}_{44.0}$	342	52.6	1.9	73.5	71.6
Comp. B	$\text{Mo}_{12}\text{V}_3\text{GeO}_{45.5}$	321	91.2	1.4	97.5	93.5
Comp. C	$\text{Mo}_{12}\text{V}_3\text{SbO}_{45.0}$	356	49.2	1.4	66.1	74.4
Comp. D	$\text{Mo}_{12}\text{V}_3\text{Cu}_{0.5}\text{NiO}_{45.0}$	341	48.2	1.5	63.6	75.8
1	$\text{Mo}_{12}\text{V}_3\text{Cu}_{0.5}\text{SbO}_{46.5}$	330	90.9	2.0	99.4	91.4

(1) 20% active component on 3/16" Alundum (α -alumina) spheres.

WHAT WE CLAIM IS:

1. A catalyst composition which comprises a catalyst having the empirical formula:



wherein X is antimony or a mixture of antimony and germanium, and wherein

a is a number from 6 to 18;

b, c and d each are 0.1 to 6; and

e is the number of oxygens required to satisfy the valence requirements of the other metals present.

2. A catalyst composition as claimed in claim 1 in which X is antimony.

3. A catalyst composition as claimed in Claim 1 in which X is a mixture of antimony and germanium.

4. A catalyst composition as claimed in any of claims 1 to 3 containing an inert support material in addition to the active catalytic ingredients.

5. A catalyst composition as claimed in any of claims 1 to 4 further containing metal oxide promoters.

6. A catalyst composition as claimed in claim 1 substantially as herein described with reference to the Examples.

7. A process for the preparation of a catalyst composition as claimed in any of claims 1 to 6 in which the catalyst-forming ingredients are mixed in predetermined proportions, if desired in the presence of a support material, and calcined.

8. A process as claimed in claim 7 in which the mixture formed is aqueous and the resulting slurry is calcined.

9. A process as claimed in claim 7 or claim 8 in which the catalyst-forming ingredients are the appropriate water-soluble salts.

10. A process as claimed in claim 7 substantially as herein described with reference to Example 4.

11. Catalyst compositions as claimed in any of claims 1 to 6 when prepared by a process as claimed in any of claims 7 to 10.

12. A process for the formation by catalytic oxidation of acrylic acid or methacrylic acid from acrolein or methacrolein with molecular oxygen in the presence of steam at a temperature of 200° to 500°C in which as catalyst there is employed a catalyst composition as claimed in any of claims 1 to 6 or 11.

13. A process as claimed in claim 12 in which acrylic acid is prepared from acrolein.

14. A process as claimed in claim 12 substantially as herein described with reference to Example 1.

15. Acrylic and/or methacrylic acid when made by a process as claimed in any of claims 12 to 14.

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